Characterization of High-Explosive Systems by Small-Angle Neutron Scattering

Joseph T. Mang (Dynamic Experimentation Division), Cary B. Skidmore (Dynamic Experimentation Division), Rex P. Hjelm (LANSCE Division), Philip M. Howe (Dynamic Experimentation Division)

Introduction

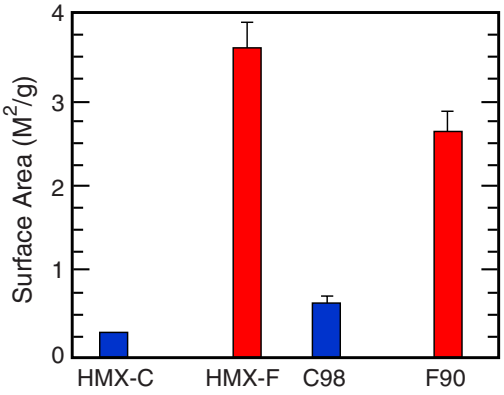
Pores (open and closed) and cracks in high-explosive (HE) materials can affect the material's response to certain stimuli such as shock. A change in pore-size distribution (and thus surface area), caused by aging or external insult, are of particular interest from both safety and performance perspectives. Small-angle neutron scattering (SANS) is a powerful tool for quantifying porosity in materials. A unique feature of the SANS technique is the ability to distinguish between open and closed porosity, allowing for more accurate measurements of total porosity and surface area.

Characterization of the microstructure of high-explosive systems is an important part of the Stockpile Stewardship Program. As microstructure plays a significant role in determining the sensitivity of an energetic material,1 detailed structural information is vital for advanced computer modeling of the properties of HE material and hence the predictability of weapon performance.

The scattering signal observed in a SANS measurement is directly related to the structure of the sample. The intensity is proportional to the number, squared volume, and the square of the difference (contrast) between the scattering length density of the material under study and that of the surrounding media. Determination of the microstructure of HE materials by SANS is complicated because each microstructural feature (crack, internal void, etc.) contributes to the total observed scattering. In such cases, an additional technique, the method of contrast variation, can be employed. The method takes advantage of the large differences in neutron scattering lengths between deuterated and non-deuterated materials. Thus, by dispersing a material in a fluid mixture containing different proportions of deuterated and non-deuterated species, the scattering length density contrast can be varied continuously and different structural features enhanced or suppressed. In this way, the scattering arising from regions accessible to the fluid (the shape ∫ external particle surfaces and surface defects) can be separated from the scattering arising from regions that are inaccessible to the fluid (the internal structure ∫ internal defects or voids). This ability allows for quantitative assessment of microstructural features and is of particular utility in studying porosity in complex materials.2 In addition, the penetrating nature of neutrons makes this technique much less invasive than other techniques (e.g. scanning electron microscopy). This allows for more direct correlation between insult and microstructural changes, a feature that is highly advantageous for future studies of damaged material. The low-Q diffractometer at the Lujan Center can provide detailed structural information (e.g. size, shape, volume fraction, etc.) over length scales between 10 and 1000 Å. For larger length scales, particle surface area can be measured.

We present SANS and contrast variation studies of the energetic materials HMX, TATB, and the HMX-based composite, PBX 9501. The purpose of these measurements was to benchmark the SANS technique against other commonly used techniques (e.g. Hg porosimetry) and to demonstrate the applicability and utility of SANS in characterizing the microstructure of HE systems. Our studies reveal systematic shifts in particle surface area and significant alteration of the size distribution of intragranular

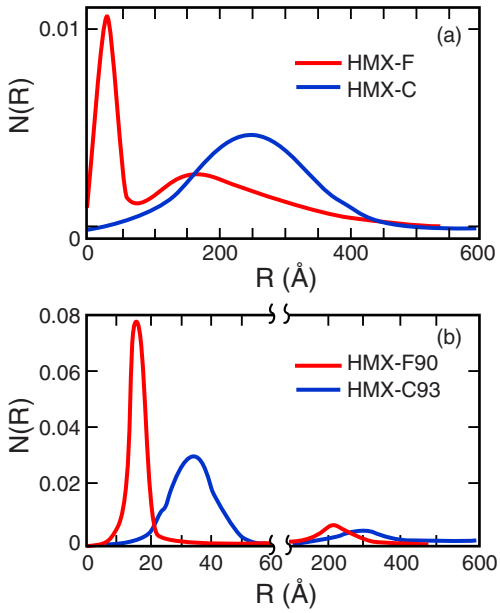
pores, both of which are dependent upon mechanical deformation.



▲ ***Fig. 1.*** *Surface area per gram derived from SANS data.*

Figure 1 displays the results of surface area analysis of shape functions obtained from SANS and contrast variation measurements. Data were obtained for both coarse (HMX-C) and fine (HMX-F, prepared by grinding HMX-C) grades of HMX as well as samples prepared by uniaxial consolidation of HMX-C (C93) and HMX-F (F90) to 93% and 90% of theoretical maximum density (TMD), respectively. As might be expected, HMX-F was found to have a much higher surface area than HMX-C because of its smaller particle size. When the coarse material was pressed, an increase of surface area was found, suggesting that pressing induces surface cracks and breaks up crystallites. However, when the fine material was pressed, a slight loss of surface area was found. This behavior can be understood by an increased surface area when crystallites are broken up or when surface cracks are induced, countered by a loss in surface area to the collapse of existing surface cracks and consolidation of individual crystallites. This same trend is seen in Hg porosimetry measurements of identically prepared samples.

Contrast variation measurements of the HMX samples revealed changes in both intensity and shape of the small-angle scattering curves. These changes indicate the presence of voids, internal (closed) to the HMX particles. In order to quantify these changes and to extract the relevant length scales, the voids were modeled as spheres. The predicted small-angle scattering from a system of polydisperse (assuming Gaussian distributions), spherical voids was fit to the measured data using a non-linear least squares algorithm. From this analysis, the number distribution, N(R), of voids having a radius between R and R + _R was extracted. Plots of N(R) are shown in Figure 2. From this figure, we see that the



▲ ***Fig. 2.*** *Internal void number distribution functions determined from model calculations.*

HMX-C sample is characterized by a single broad distribution of void dimensions, centered on R = 250Å. In comparison, the C93 sample is character ized by two distinct populations of void dimensions centered at R = 287 and 33 Å. The appearance of this new distribution of void dimensions with the application of pressure suggests that the larger voids are being squeezed out, and/or smaller-sized cracks are being induced in the material. Similar results were found for the HMX-F and F90 samples. While the HMX-F sample consisted of two distinct void populations initially, there are fewer large voids left after pressing, and the distribution of smaller-dimension voids shifts to smaller values in the F90 sample. This again suggests that the pressing squeezes out the larger voids. The polydispersity present in the current system hindered a more exact determination of the void morphology. By assuming a spherical morphology, an accurate measurement of the mean void size can be made. We anticipate that, while the use of an alternative morphology may lead to a different shape for N(R), the mean value would not change significantly.

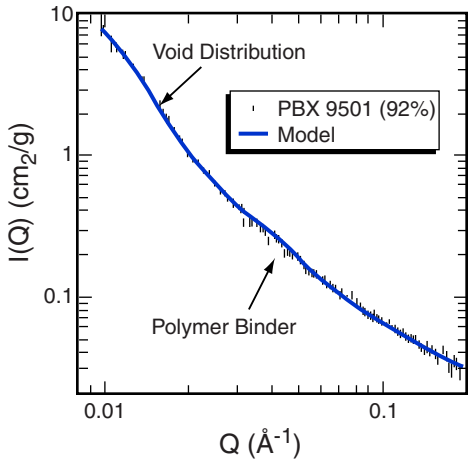
Similar measurements and analysis were performed on the energetic material TATB. Studies of TATB were conducted using four types of loose powders

prepared by both wet- (WA) and dry-amination (DA) processes as well as powders made by wet grinding of the two (UF and SF, respectively). Table I summarizes the results. As can be seen in the table, there is no significant difference between the surface area of the WA- and DA-TATB, while there is a mod est increase for SF-TATB and a large increase for UF-TATB. This trend is consistent with the results of particle-size analysis of the four powders.

Sample	Surface Area (M2/g)	Mean Void Size (Å)
WA-TATB	0.77 ± 0.08	172 ± 5
DA-TATB	0.81 ± 0.08	208 ± 1
UF-TATB	5.3 ± 0.5	59 ± 3
SF-TATB	0.94 ± 0.09	179 ± 1

▲ ***Table I.*** *Surface area and mean internal void sizes of TATB powders.*

We also see in Table I that each TATB sample can be described by a single population of internal voids. A decrease in the average size of the internal voids with grinding is seen, consistent with the HMX results.



▲ ***Fig 3.*** *Measured SANS curve from PBX 9501.*

Figure 3 shows the results of preliminary analysis of a SANS scattering curve for a PBX 9501 sample pressed to 92% of TMD. In comparison with the pre vious results, an added feature to this system is the presence of a polymer binder and the resulting HE/binder interfaces. As indicated in the figure, two distinct signals are apparent, arising from a popula tion of internal voids and the polymer binder. These results are very encouraging as they demonstrate the sensitivity of the technique to the structure of both the HE and binder components. Such sensitivi ty will be useful in future studies aimed at under standing structural changes caused by external insult and aging.

Our results demonstrate the power and utility of the SANS technique in characterizing the microstructure of HE systems. The results show that mechanical deformation, as might be encountered during pro cessing, significantly alters the HE microstructure. Future work will be directed toward the characteriza tion of damage in PBX systems.

References

1. Tarver, C., Chidester, S. and Nichols, A., J. Phys. Chem., 100, 5794 (1996).
2. Hjelm, R., Mang, J., Skidmore, C. and Gerspacher, M., Proceedings of the Workshop on Materials Research Using Cold Neutrons at Pulsed Sources Conference (World Scientific Publishing, New Jersey, USA), (in press).

Produced by the LANSCE-4 communications team: Barbara Maes, Sue Harper, Garth Tietjen, Sharon Mikkelson, and Grace Hollen.

Los Alamos
NATIONAL LABORATORY

A U.S. DEPARTMENT OF ENERGY LABORATORY
Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36.

LANSCE
Los Alamos Neutron Science Center

http://lansce.lanl.gov